Spin-orbit interactions and spin-currents from an exact-exchange Kohn-Sham method

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An exact-exchange spin-current Kohn-Sham method to treat non-collinear spin, magnetic effects, currents, spin-currents, and spin-orbit interactions self-consistently on equal footing is introduced. Spin-orbit interactions are shown to induce spin-currents. Results for silicon and germanium are presented.

The electronic structures of crystalline materials containing heavier elements are strongly affected by spin-orbit effects. Even in the band structure of germanium, a third row element, spin-orbit splittings of about 0.25 eV occur. Thus for an accurate description of electronic structures of most interesting materials a treatment of spin-orbit effects is highly desirable. If not just simple bulk semiconductors but also other materials, e.g., oxides or metals or one- and two-dimensional periodic systems like molecular wires or surfaces, shall be considered then in addition to spin-orbit effects also spin-polarization, including non-collinear spin-polarization, needs to be treated. If magnetic properties shall be studied, an inclusion of currents is necessary. In the emerging field of spintronics besides density currents also spin currents may be of importance. Materials with properties of technical interest, e.g. for new semiconductors or magnetooptical storage devices or for spintronics, often are characterized by an interplay of spin-orbit interactions, non-collinear spin-polarization, orbital currents, and spin-currents. Therefore it seems highly desirable to develop an electronic structure method that treats all of the mentioned effects in a unified way on equal footing. This work outlines such a method within the framework of density-functional theory (DFT) and, as a central result, shows how spin-orbit interactions generate spin-currents and how the latter can be treated in a self-consistent manner. As an illustration of the new method we calculate spin-orbit effects in the bandstructures of silicon and germanium with special emphasis on spin-currents induced by spin-orbit effects.

DFT is applied almost exclusively within the Kohn-Sham (KS) formalism[1]. In recent years KS methods that treat the exchange energy as well as the local multiplicative KS exchange potential exactly were developed[2,3,4,5]. Such exact-exchange (EXX) Kohn-Sham (KS) methods proved to describe the electronic structure of periodic systems, in particular bandstructures and band gaps of semiconductors, distinctively better than conventional KS methods based on the local density approximation (LDA) or generalized gradient approximations (GGAs)[2].

EXX KS methods not only yield improved bandstructures. Furthermore, they represent a systematic improvement over LDA and GGA methods in the sense that the largest fraction of the exchange-correlation functionals for energy and potential, i.e., the exchange part, no longer needs to be approximated but is treated exactly. This is crucial for the treatment of magnetic effects within DFT. Already about 20 years ago Vignale and Rasolt introduced current-spin-density-functional theory[6,7] which, in principle, enables a treatment of both spin and magnetic effects. In practice, however, current-spin-density-functional theory could not be applied to realistic systems because reliable and tractable approximate current-density functionals were not available. The EXX framework offers the opportunity to avoid at least exchange approximations and thus opens the route to current density functional methods[8,9]. Indeed, we recently presented an EXX spin-current density-functional method that is based on a spin-current density-functional theory (SCDFT)[9]. SCDFT generalizes the current spin-density-functional theory of Vignale and Rasolt by taking into account spin-currents in addition to the quantities considered in current spin-density-functional theory, i.e., the electron density, the x-, y-, z-components of the spin-density, and the x-, y-, z-components of the paramagnetic current density. The spin-currents that are additionally considered in SCDFT are the x-, y-, z-components of the paramagnetic currents of the x-, y-, z-components of the spin-density, i.e., paramagnetic currents of the magnetization.

The EXX SCDFT method enables the treatment of non-collinear spins, currents of the electron density and, going beyond current-spin-density-functional theory, spin-currents. By introducing in this work spin-orbit and scalar relativistic effects in the EXX SCDFT method the desired comprehensive description of electronic and magnetic properties of materials including relativistic effects, in particular spin-orbit effects, becomes possible.

Our starting point, the EXX SCDFT method of Ref. [9], employs basis sets of plane waves and thus requires to treat core electrons via pseudopotentials. Relativistic effects including spin-orbit splittings are generated almost exclusively in the region close to nuclei. In this region orbitals and subsequently the electronic structure is determined by the pseudopotential. In order to introduce relativistic effects, we therefore introduce spin-orbit-resolved normconserving EXX pseudopotentials $v_{\ell j}^{PP}$ with ℓ denoting the spatial orbital momentum and $j = \ell \pm 1/2$ ($j = 1/2$ for $\ell = 0$) denoting the total, i.e., spatial

plus spin, angular momentum. Instead of nonrelativistic ℓ-dependent EXX s-,p-,d-pseudopotentials we thus construct ℓj-dependent EXX $s_{1/2}$-,$p_{1/2}$-,$p_{3/2}$-,$d_{3/2}$,$d_{5/2}$-pseudopotentials that take into account all relativistic effects and employ them as separable pseudopotentials

$$v_{lj}^{sep}(\mathbf{r},\mathbf{r}') = \sum_{m=-j}^{j} \left[\int dr r^2 \phi_{lj}^\dagger(r) v_{lj}^{PP}(r)\phi_{lj}(r) \right]^{-1} \times$$
$$\times\, v_{lj}^{PP}(r)\phi_{lj}(r)\Omega_{ljm}(\hat{\mathbf{r}}) v_{lj}^{PP}(r')\phi_{lj}(r')\Omega_{ljm}^\dagger(\hat{\mathbf{r}}'). \quad (1)$$

In Eq.(1) the Ω_{ljm} denote central field spinors, i.e., two-component angular momentum eigenfunctions with total angular momentum j and corresponding magnetic quantum number m that result from angular momentum coupling of spin eigenfunctions with quantum numbers $s = 1/2$ and $m_s = \pm 1/2$ represented by two dimensional unit vectors and spherical harmonics with quantum numbers ℓ and m_ℓ. The pseudopotentials $v_{\ell j}^{PP}$ are constructed in such a way that the valence orbitals resulting from a pseudopotential EXX calculation for the atom, i.e., the atomic pseudoorbitals ϕ_{lj}, are identical to the large components of the valence orbitals from a fully relativistic all electron EXX calculation beyond the radius r_c and have the same eigenvalues.

The KS Hamiltonian operators of the pseudopotential EXX calculation for the atom and of the final plane wave EXX-SCDFT calculation are nonrelativistic except that they contain the pseudopotentials $v_{\ell j}^{PP}$. The latter introduce the relativistic effects in particular the spin-orbit interaction. As a result the plane wave EXX-SCDFT calculation then differs from a standard nonrelativistic pseudopotential EXX calculation not only by the fact that the orbitals are two-dimensional spinors that contain spin-up and spin-down components which, in general, both are nonvanishing, but in addition by the coupling of the two spin components through the the ℓj-dependent pseudopotentials. The latter are obtained along the lines described in Ref. [10,11], however, without averaging the two lj-dependent pseudopotentials v_{lj}^{PP} with $j = \ell - 1/2$ and $j = \ell + 1/2$.

Technically we construct lj-dependent pseudopotentials $v_{\ell j}^{PP}$ for a fully relativistic four-component pseudopotential calculation. The corresponding pseudoorbitals occuring in the separable pseudopotentials v_{lj}^{sep} of Eq. (1), at first, are four-component spinors. We then use only the renormalized large components ϕ_{lj} of the original four-component pseudoorbitals to construct separable pseudopotentials v_{lj}^{sep} for a two-component valence-electron calculation that takes into account relativistic effects only through the pseudopotentials. Strictly speaking this is somewhat inconsistent. However, the charge of the pseudoatoms is very low, for Si and Ge just 4 a.u. and it is save to assume that direct relativistic effects, i.e., relativistic effects that do not have their origin in the pseudopotential, but would result from a fully relativistic four-component treatment of the valence electrons, are negligible for such small effective

nuclear charges. Indeed for the atoms Si and Ge the energetic differences from a two-component pseudopotential calculation and a fully relativistic four-component pseudopotential calculation are of the order of μHartree and thus completely negligible.

In order to analyze how relativistic effects are taken into account in a EXX SCDFT calculation via the j-dependent pseudopotentials $v_{\ell j}^{PP}$ constructed with the relativistic EXX approach[10,11], we consider for the moment the KS orbitals of a bulk system as linear combinations of atomic pseudoorbitals ϕ_{lj}. One effect of the relativistic pseudopotentials is that s- and p-orbitals are contracted and lowered in energy while d- and f-orbitals are more diffuse and raised in energy. The influence of these effects on the KS orbitals in the bulk are automatically taken into account in a standard EXX treatment. The j-dependence of the pseudopotentials, which is a consequence of spin-orbit interactions, on the other hand, as mentioned above, leads to two-dimensional spinors as orbitals and causes features not present in standard EXX methods, like spin-currents.

For a more detailed discussion of the effect of spin-orbit interactions and in particular of the generation of spin-currents we consider a two-component all-electron Pauli-Hamiltonian operator of an electronic system in a magnetic field including spin-orbit interactions:

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{v}_{ext} + \hat{H}^{mag} + \hat{H}^{SO}$$
$$= \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} \left[v_{ext}(\mathbf{r}_i) + \tfrac{1}{2}\mathbf{p}_i\cdot\mathbf{A}(\mathbf{r}_i) + \tfrac{1}{2}\mathbf{A}(\mathbf{r}_i)\cdot\mathbf{p}_i \right.$$
$$\left. +\tfrac{1}{2}\mathbf{A}(\mathbf{r}_i)\cdot\mathbf{A}(\mathbf{r}_i) + \tfrac{1}{2}\,\boldsymbol{\sigma}\cdot\mathbf{B}(\mathbf{r}_i) + \tfrac{1}{4c^2}\,\boldsymbol{\sigma}\cdot[(\nabla v_{ext})(\mathbf{r}_i)\times\mathbf{p}_i] \right]$$
$$= \hat{T} + \hat{V}_{ee} + \int d\mathbf{r}\ \boldsymbol{\Sigma}^T\,\mathbf{V}(\mathbf{r})\,\hat{\mathbf{J}}(\mathbf{r}). \quad (2)$$

In Eq. [2], $\hat{T}$ and $\hat{V}_{ee}$ are the operators of the kinetic energy and the electron-electron repulsion, $\hat{v}_{ext}$ is the operator generated by the external electrostatic potential v_{ext}, usually the potential of the nuclei, $\hat{H}^{mag}$ are the parts of the Hamiltonian operator caused by a magnetic field $\mathbf{B}$ with accompanying vector potential $\mathbf{A}$, and $\hat{H}^{SO}$ describes the spin-orbit interaction. By $\mathbf{r}_i$ the position of the i-th electron is denoted, by $\mathbf{p}_i$ the corresponding canonical momentum operator. The vector $\boldsymbol{\sigma}$ contains the Pauli spin matrices. The sum in the first line of Eq. [2] runs over all N electrons. The vector $\boldsymbol{\Sigma}$ has four components, Σ_0 being a 2x2 unit matrix and Σ_1, Σ_2, and Σ_3 being the Pauli spin matrices $\boldsymbol{\sigma}_x$, $\boldsymbol{\sigma}_y$, and $\boldsymbol{\sigma}_z$. The four components of the vector $\hat{\mathbf{J}}(\mathbf{r})$ are the density operator $\sum_{i=1}^{N}\ \delta(\mathbf{r}-\mathbf{r}_i) = \hat{J}_0(\mathbf{r})$ and the x-, y, z- components of the current operator $\left(\tfrac{1}{2}\right)\sum_{i=1}^{N}\ p_{x,i}\ \delta(\mathbf{r}-\mathbf{r}_i) + \delta(\mathbf{r}-\mathbf{r}_i)\ p_{x,i} = \hat{J}_1(\mathbf{r})$ etc. The 4x4 matrix $\mathbf{V}(\mathbf{r})$ is composed of matrixelements $V_{\mu\nu}(\mathbf{r})$

with $\mu, \nu = 0, 1, 2, 3$ and is given by

$$\mathbf{V}(\mathbf{r}) = \begin{pmatrix} v_{ext}(\mathbf{r}) + \frac{\mathbf{A}^2(\mathbf{r})}{2} & A_x(\mathbf{r}) & A_y(\mathbf{r}) & A_z(\mathbf{r}) \\ \frac{B_x(\mathbf{r})}{2} & 0 & -\frac{v_{ext,z}(\mathbf{r})}{4c^2} & \frac{v_{ext,y}(\mathbf{r})}{4c^2} \\ \frac{B_y(\mathbf{r})}{2} & \frac{v_{ext,z}(\mathbf{r})}{4c^2} & 0 & -\frac{v_{ext,x}(\mathbf{r})}{4c^2} \\ \frac{B_z(\mathbf{r})}{2} & -\frac{v_{ext,y}(\mathbf{r})}{4c^2} & \frac{v_{ext,x}(\mathbf{r})}{4c^2} & 0 \end{pmatrix}. \tag{3}$$

In Eq. [3], $v_{ext,x}(\mathbf{r}) = \partial v_{ext}(\mathbf{r})/\partial x$. The fact that the spin-orbit interaction Hamiltonian operator $\hat{H}^{SO}$ can be expressed according to the last line of Eq. [2] together with Eq. [3] is crucial, because this represents the basis for the SCDFT recently introduced in Ref. [9]. The spin-orbit interaction only leads to additional terms in the matrix $\mathbf{V}$ of Eq. [3], which do not interfere with the derivation of the SCDFT of Ref. [9], i.e., the latter derivation also holds in the presence of the spin-orbit Hamiltonian operator $\hat{H}^{SO}$.

According to Ref. [9] the many-electron KS equation associated with a Schrödinger equation with an Hamiltonian operator given by Eq. [2] is determined by the KS Hamiltonian operator

$$\hat{H}_s = \hat{T} + \int d\mathbf{r} \; \boldsymbol{\Sigma}^T \, \mathbf{V}_s(\mathbf{r}) \, \hat{\mathbf{J}}(\mathbf{r}) \tag{4}$$

with the 4x4 matrix $\mathbf{V}_s$ representing the KS potential, which is given by $\mathbf{V}_s(\mathbf{r}) = \mathbf{V}(\mathbf{r}) + \mathbf{U}(\mathbf{r}) + \mathbf{V}_{xc}(\mathbf{r})$. The Hartree potential $\mathbf{U}$ and the exchange-correlation potential $\mathbf{V}_{xc}$ can be represented by 4x4 matrices. Within the matrix $\mathbf{U}$ only the component $U_{00}(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho_{00}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$, the standard Hartree potential, is different from zero. The components $\mathbf{V}_{xc,\mu\nu}$ of the exchange-correlation potential $\mathbf{V}_{xc}$ are given by

$$V_{xc,\mu\nu}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \rho_{\mu\nu}(\mathbf{r})}. \tag{5}$$

Within the considered SCDFT all 16 components of the spin-current density $\boldsymbol{\rho}$ of the KS system equal those of the real electronic system. The components $\rho_{\mu\nu}$ with $\mu, \nu = 0, 1, 2, 3$ of $\boldsymbol{\rho}$ are defined as follows: ρ_{00} is just the regular ground state electron density, $\rho_{\mu 0}$ with $\mu = 1, 2, 3$ represent the x-, y-, and z-components of the spin-density, $\rho_{0\nu}$ with $\nu = 1, 2, 3$ represent the x-, y-, and z-components of the paramagnetic current of the electron density, while $\rho_{\mu\nu}$ with $\mu, \nu = 1, 2, 3$ represent the components of the paramagnetic currents of the spin-density, i.e., currents of the magnetization.

In the absence of spin-orbit interactions a correct description of all 16 components of the spin-current density $\boldsymbol{\rho}$ through the KS system is desirable for systems that exhibit non-vanishing currents of the spin-density, similarly as it is desirable in standard, i.e., non-current, density-functional theory to treat spin-polarized systems within spin-density-functional theory in order to correctly describe both spin-up and spin-down electron densities. However, in the absence of spin-orbit interactions, the Hamiltonian operator Eq. (2) does not couple to currents of the spin-density, i.e., does not couple to $\rho_{\mu\nu}$ with $\mu, \nu = 1, 2, 3$. Therefore it is possible in these cases to apply the standard current spin-density formalism of Vignale and Rasolt, which considers only the ground state electron density, ρ_{00}, the spin-density $\rho_{\mu 0}$ with $\mu = 1, 2, 3$, and the paramagnetic current of the electron density $\rho_{0\nu}$ with $\nu = 1, 2, 3$, similarly as it is possible to treat spin-polarized systems via non-spin-polarized density-functional theory although this might affect the accuracy in practical application, which require the use of approximate density-functionals. In the presence of spin-orbit interactions the situation is different. Because the Hamiltonian operator [2] now couples to components of the paramagnetic currents of the spin-density it is mandatory that the KS system correctly describes all 16 components of the spin-current density $\rho_{\mu\nu}$, i.e., the standard current spin-density functional formalism is no longer applicable in the presence of spin-orbit interactions.

In our case we do not treat spin-orbit interactions by the explicit spin-orbit term H^{SO} of Eq. (2), but via the j-dependent pseudopotentials v_{lj}^{sep} of Eq. (1). However, j-dependent pseudopotentials, by construction, generate an effect corresponding to that of the spin-orbit term H^{SO} and thus like the latter generate spin-currents and couple to them. It is important to notice that spin-currents, due to the continuity of orbitals, are present not only close to the nuclei, but also in the interstitial region between the atoms despite the fact that they are generated close to the nuclei by pseudopotentials. Thus spin-currents affect the bonding and generally the electronic structure. A full and self-consistent treatment of the effects of spin-currents in DFT therefore requires a spin-current density-functional treatment as provided by the EXX SCDFT method of this work.

Note that an explicit treatment of spin-orbit interactions via H^{SO} in a selfconsistent KS method would be problematic, because the spin-orbit term H^{SO} arising from the relativistic many-electron Hamiltonian operator via the singular Wouldy-Wouthausen transformation leads to severe instabilities. Two-component methods that do not employ pseudopotentials therefore treat spin-orbit effects either perturbatively[12] or within methods based on two-component Hamiltonian operators obtained by other transformation like the Douglas-Kroll-Hess transformation[13].

In the proposed combination of spin-orbit resolved j-dependent pseudopotentials with the EXX-SCDFT method[9] we treat the exchange contribution $\mathbf{V}_x$ of the required exchange-correlation potential $\mathbf{V}_{xc}$ exactly and neglect the correlation contribution. An inclusion of an approximate LDA or GGA correlation potential for the component $V_{c,00}$ would be straightforward. However, experience from standard EXX calculations shows that the inclusion of an LDA or GGA correlation potential has only marginal effect on the bandstructure.

For the self consistent solid state calculations plane wave energy cutoffs of 25 Ry for the orbitals and 14 Ry for the KS response function were chosen. The set of used
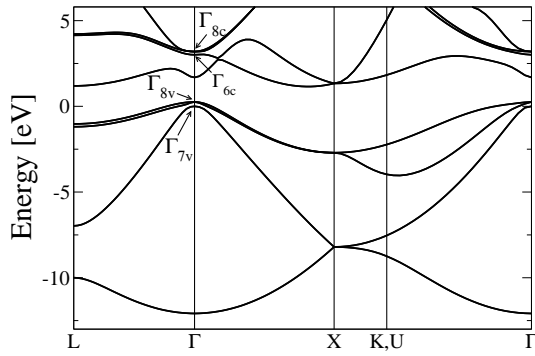
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